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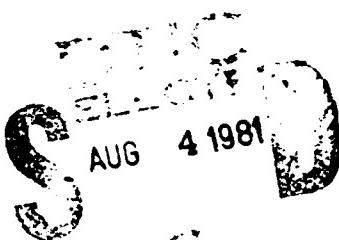
FRANK J. SEILER RESEARCH LABORATORY

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JUNE 1981

ATTEMPTED FLUORINATION OF NITROAROMATICS
BY XENON DIFLUORIDE

BY



NEAL M. ELY

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Neal M Ely
NEAL M. ELY, Captain USAF
Project Scientist

Armand A. Fannin, Jr.
ARMAND A. FANNIN, JR., Lt Colonel, USAF
Director, Chemical Sciences

WILLIAM D. SIURU, JR.
WILLIAM D. SIURU, JR., Lt Colonel, USAF
Commander

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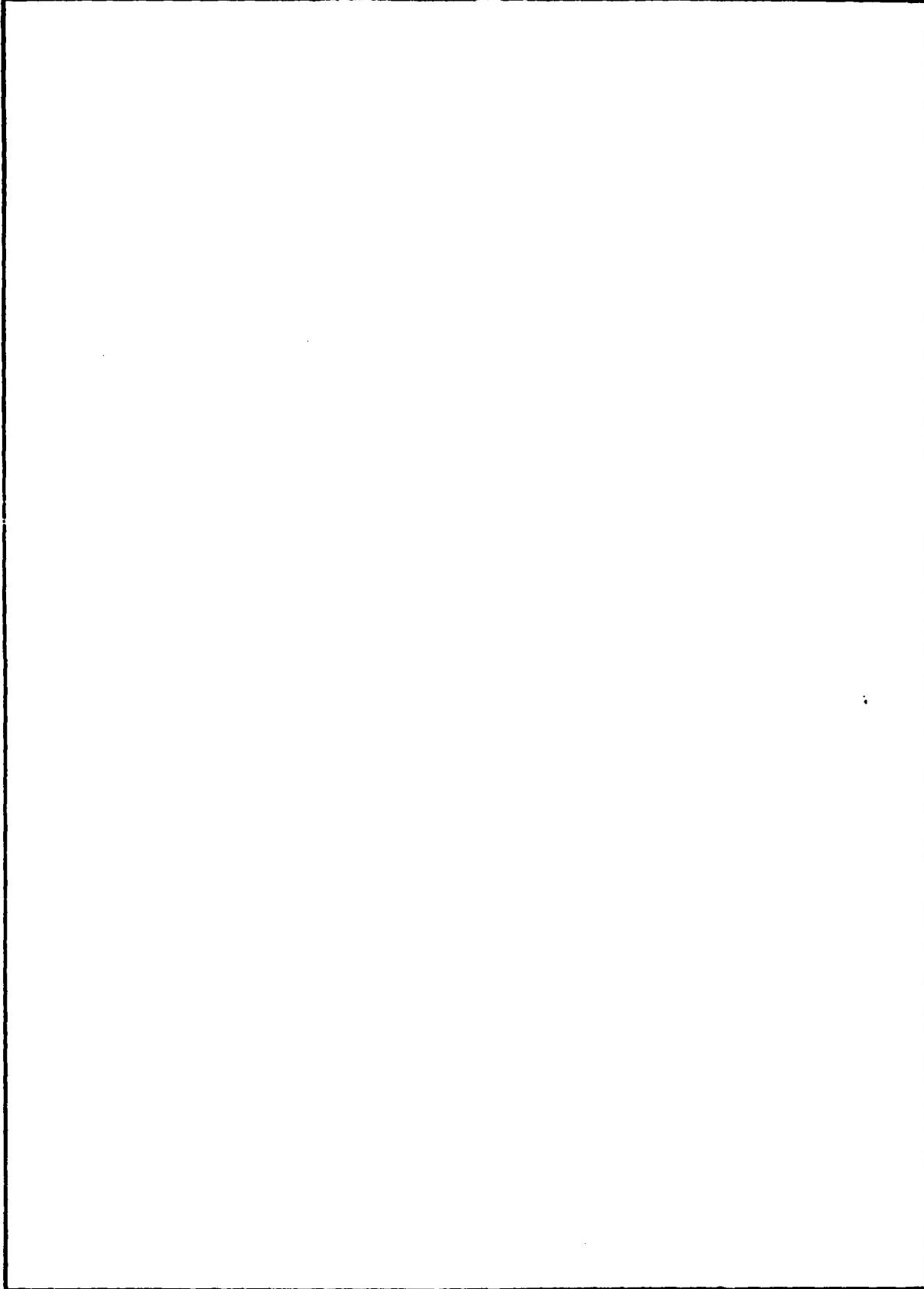
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SUMMARY

The attempted fluorination of nitroaromatics using xenon difluoride as the fluorinating agent is discussed. Failures with di and trinitro compounds and success with p-nitrotoluene are described.

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INTRODUCTION

Selective fluorination of organic compounds by xenon difluoride has become well established in recent years¹. The research at Frank J. Seiler has been centered on using boron trifluoride etherate or light to catalyze or initiate fluorinations by $XeF_2^{2,3}$. The intent of this project was to use XeF_2 as a means of fluorinating energetic nitroaromatics such as trinitrotoluene (TNT) by substitution on the aromatic ring (as opposed to the methyl group protons).

The replacement of hydrogen by fluorine in energetic compounds generally increases the thermal stability of these compounds, their density, and their oxygen balance. This leads to improved energetic properties of these compounds. Since the energy released during a detonation is proportional to the square of an explosives' initial density, higher initial density allows more energy release during detonation. Also, since many munitions are volume limited for explosive capacity, a higher density would allow a greater amount of explosive to be loaded in the volume in a munitions item. Studies of munitions carried externally at supersonic speeds (TAF-ROC-306-75) have shown the need for energetic materials with increased thermal stability.

Because of its wide use in munitions, TNT seemed a good candidate to begin with. Unfortunately, as will be discussed later, this was not the case.

EXPERIMENTAL

XeF_2 was prepared by slight modification of the high-pressure mercury arc lamp irradiation technique⁴. The boron trifluoride etherate (Eastman Organic Chemicals, practical grade) was vacuum distilled to a colorless

liquid prior to use⁶. TNT⁶, 2,4-dinitroaniline (picramide)⁷ were prepared according to published procedures. Hexane and methylene chloride were distilled from NaOH and stored over 4A molecular sieves while acetonitrile was distilled from P_2O_5 prior to storing over 4A molecular sieves. p-Nitrotoluene (Eastman Organic Chemicals), 2,6-dinitrotoluene (Aldrich) and 2,4-dinitrotoluene (Matheson Coleman and Bell) were used as received without further purification. Diethyl ether (Mallinckrodt AR) was distilled from zinc boron/benzophenone prior to use and CCl_4 was distilled from LiAlH₄ and stored over 4A molecular sieves.

Storage and manipulation of XeF_2 were done in a dry box with a purified nitrogen atmosphere kept at less than 10 ppm combined H_2O and O_2 . Mass spectra were recorded on either a duPont 21-491 dual beam mass spectrometer or Hewlett Packard 5990A or 5985 GC mass spectrometers. NMR spectra were recorded on a Varian T-60 spectrometer.

2-fluoro-4-nitrotoluene. XeF_2 (0.3g, 1.77 mmol) and p-nitrotoluene (0.12g, 0.88 mmol) were weighed into a 50 ml round bottom flask in the dry box, cooled to 0°C and 25 mL of CH_2Cl_2 was added. Stirring was begun and the solid materials dissolved to give a colorless solution. $BF_3 \cdot OEt_2$ (1 mL, .81 mmol) was then added slowly via syringe and the solution immediately took on a lemon yellow color which darkened during the next 10 minutes. The reaction was allowed to proceed at 0°C for 1.5 hours and then at room temperature (RT) for 3 more hours. At this time, an aliquot was taken for analysis - gas chromatography-mass spectrometry (GC/MS). Based on the spectra, 2-Fluoro-4-nitrotoluene was the main product present (70% yield)⁸.

Attempt to fluorinate 2,6-dinitrotoluene (2,6-DNT). XeF_2 (0.2g, 1.2 mmol) and 2,6-dinitrotoluene (0.1 g, 0.8 mmol) were weighed into a

50 ml round bottom flask in the dry box. 25 ml of acetonitrile was added to dissolve the solids, giving a colorless solution. The $\text{BF}_3 \cdot \text{OEt}_2$ (.15 ml, 1.23 mmol) was injected and the reaction solution gradually turned yellow accompanied by the evolution of gas. After stirring for 3 hours at RT, an aliquot was taken for analysis by GC/MS. The only compound detected was 2,6-DNT. The reaction was then refluxed for two days, but analysis by GC/MS still revealed only 2,6-DNT.

Attempt to fluorinate 2,4-dinitrotoluene (2,4-DNT). XeF_2 (0.49g, 2.87 mmol) and 2,4-DNT (.25g, 1.37 mmol) were weighed into a 50 ml round bottom flask in the dry box. This flask was removed from the dry box, cooled to 0°C and 25 ml of CH_2Cl_2 was added. The solids dissolved upon stirring to give a colorless solution. $\text{BF}_3 \cdot \text{OEt}_2$ (0.16 ml, 1.4 mmol) was added dropwise via syringe, which caused the solution to turn yellow almost immediately. The reaction was warmed to RT and allowed to stir for 2 days. Analysis of an aliquot by GC/MS indicated that the only species present in solution was 2,4-DNT.

Reaction of TNT and XeF_2 . Type I. In a typical reaction⁹, XeF_2 (0.45g, 2.64 mmol) was weighed into a 50 ml round bottom flask in the dry box. 15 ml of diethyl ether was distilled onto the XeF_2 and the mixture was cooled to 0°C with stirring. TNT (0.3g, 1.32 mmol) was weighed into another round bottom flask and 20 ml of diethyl ether was added and stirred until the TNT dissolved. The TNT solution was transferred into the XeF_2 solution. Then 0.22g (1.55 mmol) of $\text{BF}_3 \cdot \text{OEt}_2$ in 5 ml of diethyl ether was added dropwise from an addition funnel to the reaction solution. The clear colorless reaction solution was stirred at 0°C for three hours during which time it had become pale yellow in color. The reaction was

then warmed to RT and stirred for 1 hour. An aliquot examined by GC/MS was found to contain only TNT. Stirring continued during which time a black precipitate began to form with the solution darkening noticeably. After stirring for 48 hours the reaction solution was again examined by GC/MS which revealed only TNT present in solution (it should be noted that a very small peak of 0.7% abundance and m/e of 281 did appear in the spectrum). The reaction solution was filtered and the black precipitate was washed thoroughly with acetone and dried. The amber acetone washing was evaporated until a brown solid remained. Examination of both the brown and black solids by NMR revealed only TNT present as well as some material containing an ethyl moiety.

Reaction of TNT and XeF₂. Type II. XeF₂ (0.2g, 1.18 mmol) was dissolved in 10 ml of CH₃CN in a two neck round bottom flask. A N₂ inlet was coupled to one neck and an addition funnel containing TNT (.14g, 0.6 mmol) dissolved in 15 ml of CH₃CN was coupled to the other neck. This apparatus was irradiated for two minutes by a 750 watt Hanovia mercury lamp. Then, with irradiation continuing, the TNT/CH₃CN solution was added dropwise slowly to the XeF₂/CH₃CN solution with stirring. Irradiation continued for 1 hour. At this point, an aliquot was taken for examination by GC/MS. The spectrum revealed that only TNT was present in the solution.

Reaction of TNT and XeF₂. Type III. XeF₂ (0.3g, 1.77 mmol) and TNT (0.2g, 0.8° mmol) were weighed into a 50 ml round bottom flask equipped with a small glass inlet tube fitted with a rubber septum. This flask was immersed in an oil bath at 100°C and stirring was begun of the molten reaction mixture. BF₃·OEt₂ (0.12g, 0.84 mmol) was injected through the septum. The reaction turned very dark brown immediately. After stirring

at 100°C for 3 hours, a small amount of the reaction mixture was taken for analysis by GC/MS. The only identifiable compound present in significant abundance was TNT.

Reaction of XeF₂ and picramide. XeF₂ (0.17g, 1 mmol) and picramide (0.1g, 0.44 mmol) were weighed into a 50 ml round bottom flask. 25 ml of acetonitrile was added and stirring begun. The solids dissolved to give a yellow solution. BF₃·OEt₂ (0.07g, 0.5 mmol) was syringed in and the reaction turned golden immediately and the evolution of gas bubbles was observed. After stirring for 3 hours at RT, an aliquot was taken for examination by GC/MS. The only substance detected was picramide

RESULTS AND DISCUSSION

Fluorination of nitroaromatics by XeF₂ worked well when one nitro group was present. However, the presence of two or more nitro groups on the aromatic ring resulted in the starting organic compound being left essentially unreacted. This can be attributed to the strong deactivating effect that the nitro group has towards electrophilic aromatic substitution. Apparently, two or more nitro groups leave the ring essentially unreactive towards fluorination by XeF₂.

Fluorination of p-nitrotoluene proceeded fairly smoothly, giving 2-fluoro-4-nitrotoluene as the major product in 70% yield (by mass spectral analysis). All attempts to fluorinate 2,6- and 2,4-dinitrotoluene failed. It should be noted that in one reaction with XeF₂ and 2,4-dinitrotoluene, a small peak (less than 2% abundance) was observed in the GC/MS which might be attributable to a fluorinated dinitrotoluene.

Numerous attempts to fluorinate TNT met with consistent failure, even under fairly harsh reaction conditions. There was no evidence in any of

the GC/MS data that suggested a fluorinated TNT had been formed. Some mass spectra data from a type II reaction suggested that a small amount of a compound was formed where a fluoride had replaced a nitro group on the ring. No attempt was made to isolate this due to the small amount present in solution.

An attempt was made to increase the reactivity of the ring by using a substituent more activating than the methyl group. In this vein, picramide was tried instead of TNT, however, it, as was the case with TNT, failed to be fluorinated by XeF_2 .

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- (8) Precise identity of the compound was based on comparison with the mass spectrum of an actual sample of 2-fluoro-4-nitrotoluene.
- (9) Similar results were obtained using CCl_4 and CH_2Cl_2 and also when the stoichiometry of the reactants and catalysts was varied.

**DAU
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